

A NOVEL HYDRINDANE SYNTHESIS

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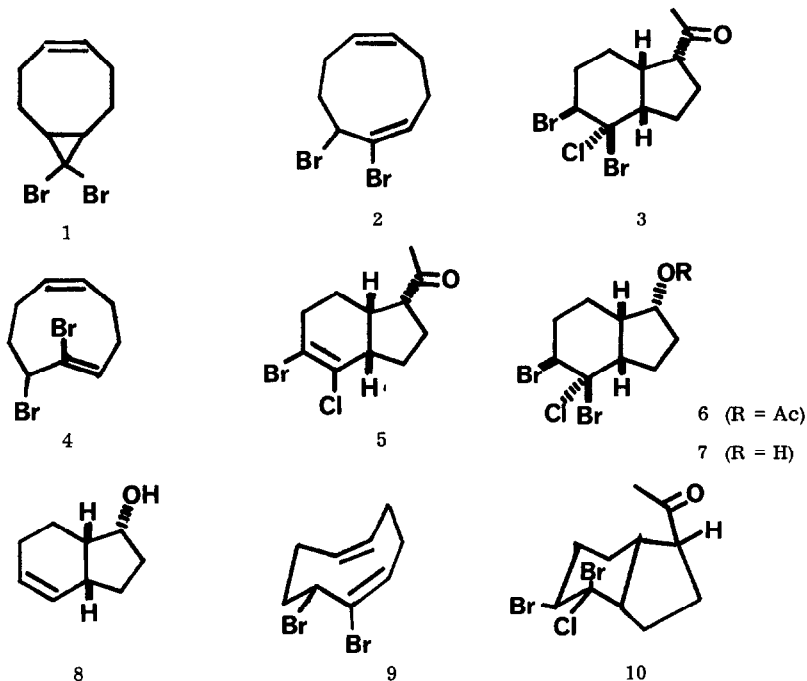
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Reaction of the dibromide¹ (1) with acetic anhydride-zinc chloride in methylene chloride yielded the dibromide² (2) (21%) and the crystalline ketone (3) (30%), ν_{\max} 1710 cm^{-1} , τ (CDCl_3) 7.85 (3Hs), 5.80 (1H $W_{\frac{1}{2}}$ 22Hz). The same products were obtained in the same proportions when (1) was replaced by the isomers (2) or (4). Dehydrobromination of (3) using sodium ethoxide or 1,5-diazobicyclo[4.3.0]non-5-ene yielded the olefin (5), ν_{\max} 1710, 1620 cm^{-1} , τ (CDCl_3) 7.93 (3Hs). Baeyer-Villiger oxidation of (3) with m-chloroperbenzoic acid in chloroform generated the acetate (6) ν_{\max} 1725 cm^{-1} , τ (CDCl_3) 8.03 (3Hs), 6.00 (1Hm) which was hydrolysed to the alcohol (7), ν_{\max} 3350 cm^{-1} , τ (CDCl_3) 5.7 - 6.5 (3H). Oxidation of (7) with Jones' reagent at -20° gave the corresponding ketone, ν_{\max} 1745 cm^{-1} , τ (CDCl_3) 5.90 (1Hm), which on reduction with lithium in ammonia yielded a single alcohol (8), ν_{\max} 3350, 675 cm^{-1} , τ (CDCl_3) 4.4 (2Hm), 6.0 - 6.7 (2H). Catalytic hydrogenation of (8) gave a cis-hydrindan-1-ol which was oxidized to the corresponding ketone, found to be identical with an authentic sample prepared by catalytic hydrogenation of 4,5,6,7-tetrahydroindan-1-one³. These results establish the constitution of (3) except for the position of the -CHBrCBrCl- unit which is assigned by considering the probable mechanism of formation of (3).

When (1) was reacted with zinc chloride in methylene chloride it was isomerised to the trans-olefin (4) but little or none of the cis-compound (2) was formed. However, addition of a trace of acetic anhydride brought about the second isomerisation to (2). This could be a solubility effect since the first isomerisation occurs in a heterogeneous system. There seems little doubt that it is (2) which undergoes the cation initiated cyclisation. (9) is a reasonable conformation for (2) and if it is the reacting conformation the structure and stereochemistry depicted for (3) follows.

The dominant conformation of (3) is most likely to be (10) since the alternative would have a serious 1,3-diaxial interaction. If so then trans-diaxial elimination to form (5) suggests that the geminal dihalide unit has Br axial and Cl equatorial.

Here again the high stereoselectivity observed in the cyclisation of medium-ring compounds is demonstrated⁴. A stereochemically similar cyclisation has been discovered with cis, cis-cyclonona-1,5-diene⁵ and Friedel-Crafts acylation of cis, cis-cycloocta-1,5-diene⁶ also leads to transannular cyclisation.



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